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OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS
REPORT

for

Grant N00014-91-J-1447

R&T Code 4134044

**OMVPE Growth of InAsSbBi and Related Alloys Using New
Organometallic Group V Sources**

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Summary of Activities During the Last 3 Years.

- a. Number of papers submitted, unpublished: 5.
- b. Number of papers in refereed journals: 13.
- d. Number of book chapters published: 2.
- h. Number of invited presentations at professional meetings: 9.
- i. Number of presentations at professional meetings: 6.
- j. Honors/Awards/Prizes: 12.
- k. Number of students supported: 5.
(no minority or female students, 4 Asian graduate students)



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Part I Papers Written Between 2/1/88 and 4/30/91 (Supported Exclusively by ONR Unless Indicated).

a. Papers Submitted to Refereed Journals (not yet published)

Effect of Growth Temperature on Photoluminescence of InAs Grown by OMVPE (Z.M. Fang, K.Y. Ma, R.M. Cohen, and G.B. Stringfellow), Appl. Phys. Lett. (accepted).

Investigation of Organometallic Vapor Phase Epitaxial of InAs and InAsBi at Temperatures as Low as 275°C, (K.Y. Ma, Z.M. Fang, R.M. Cohen, and G.B. Stringfellow), J. Appl. Phys. (accepted)

OMVPE Growth of AlGaSb and AlGaAsSb, (D.S. Cao, Z.M. Fang, and G.B. Stringfellow), J. Crystal Growth (accepted).

Triisopropylantimony for OMVPE of GaSb and InSb, (C.H. Chen, Z.M. Fang, and G.B. Stringfellow), Appl. Phys. Lett. (accepted)

Decomposition Studies of Triisopropylantimony and Triallylantimony, (S.H. Li, C.A. , R.W. Gedridge, and G.B. Stringfellow), J. Electron. Mater. (accepted)

b. Papers Published in Refereed Journals

The Use of Triisopropylantimony for the Growth of InSb and GaSb, (C.H. Chen, Z.M. Fang, and G.B. Stringfellow), J. Appl. Phys. **69**, 7605 (1991).

Raman Scattering in AlGaAsSb Quaternary Alloys (D.H. Jaw , D.S. Cao, and G.B. Stringfellow), J. Appl. Phys. **69**, 2552 (1991)

Decomposition Mechanisms of TVSb and Reactions with TMGa (C.A. Larsen, R.W. Gedridge, and G.B. Stringfellow) Chemistry of Materials **3**, 96 (1991).

OMVPE Growth and Characterization of Bi-Containing III/V Alloys, (K.Y. Ma, Z.M. Fang, R.M. Cohen, and G.B. Stringfellow), J. Crystal Growth **107**, 416 (1991).

Photoluminescence of InAsBi and InAsSbBi Grown by OMVPE , Z.M. Fang, K.Y. Ma, D.H. Jaw, R.M. Cohen, and G.B. Stringfellow, J. Appl. Phys. 68, 1187 (1990).

Organometallic Vapor Phase Epitaxy Growth and Characterization of Bi-containing III/V Alloys , K.Y. Ma, Z.M. Fang, R.M. Cohen, and G.B. Stringfellow, J. Appl. Phys. 68 4586 (1990).

Dimethylarsine: Pyrolysis Mechanisms and Use for OMVPE Growth, S.H. Li, C.A. Larsen, C.H. Chen, G.B. Stringfellow, and D.W. Brown, J. Electron. Mater. 19 299 (1990).

Photoluminescence of InSb, InAs, and InAsSb Grown by Organometallic Vapor Phase Epitaxy, Z.M. Fang, K.Y. Ma, D.H. Jaw, R.M. Cohen, and G.B. Stringfellow, J. Appl. Phys. J. Appl. Phys. 67 7034 (1990).

Alternate Sources and Growth Chemistry for OMVPE and CBE Processes, G.B. Stringfellow, J. Crystal Growth 105 260 (1990). (Department of Energy and ONR support).

Organometallic Vapor Phase Epitaxial Growth and Characterization of InAsBi and InAsSbBi, G.B. Stringfellow, W.P. Kosar, and D.W. Brown, K.Y. Ma, Z.M. Fang, D.H. Jaw, R.M. Cohen, Appl. Phys. Lett. 55, 2420 (1989).

OMVPE Growth of GaAs Using Dimethylarsine, C.H. Chen, E.H. Reihlen, and G.B. Stringfellow, J. Crystal Growth 96, 497 (1989).

Raman Scattering in InAsSb Grown by Organometallic Vapor Phase Epitaxy, Y.T. Cherng, K.Y. Ma, and G.B. Stringfellow, Appl. Phys. Lett. 53 886 (1989).

Long-Range Order in InAsSb, H.R. Jen, K.Y. Ma, and G.B. Stringfellow, Appl. Phys. Lett. 54 1154 (1989). (Department of Energy and ONR support).

d. Papers Published in Books

Decomposition Mechanisms of Antimony Source Compounds for OMVPE, C.A. Larsen, R.W. Gedridge, S.H. Li, and G.B. Stringfellow),

chemical Perspectives of Microelectronic Materials - II (Materials Research Society, Pittsburg, Penn, 1991), pp. 129-134.

Non-hydride Group V Sources for OMVPE, G.B. Stringfellow, in *III/V Heterostructures for Electronic/Photonic Devices* ed. C.W. Tu, V.D. Matters, and A.C. Gossard (Materials Research Society), 171 (1989).(AFOSR and ONR support).

h. Invited Presentations at Topical or Scientific/Technical Society Conferences

New Sources for OMVPE, 10th Symposium on Alloy Semiconductor Physics and Electronics, July 18-19, 1991, Nagoya, Japan (Plenary Talk).

Fundamental Aspects of Vapor Growth and Epitaxy, 7th International Conference on Vapor Growth and Epitaxy, July 15-17, 1991, Nagoya, Japan (Plenary Talk).

Reactions Occurring During OMVPE of III/V Semiconductors, 200th American Chemical Society National Meeting, Washington, D.C., August 26-31, 1990.

Alternate Sources and Growth Chemistry for OMVPE and CBE Processes, 2nd International Conference on Chemical Beam Epitaxy, Houston, December, 1989. (AFOSR and ONR support).

Mechanistic Studies of Organometallic Vapor Phase Epitaxy, 1st International Conference on Epitaxial Crystal Growth, Budapest, Hungary, April 1990. (AFOSR and ONR support).

Alternate Group V Sources for OMVPE, American Institute of Chemical Engineers 1989 Annual Meeting, San Francisco, November 1989.

Reaction Mechanisms for OMVPE Growth of III/V Semiconductors, American Association for Crystal Growth/West Conference on Crystal Growth, Lake Tahoe, CA, June, 1989. (AFOSR and ONR support) (AFOSR and ONR support).

Non-Hydride Group V Sources for OMVPE, invited paper presented at the Spring Materials Society Meeting, San Diego, CA, April 1989.(AFOSR and ONR support).

OMVPE for Metastable Alloys and Natural and Artificially Structured Materials, Workshop on Materials Science of Epitaxial Heterostructures, Monterey, Ca, January 9-14, 1989.(Department of Energy and ONR support).

i. Contributed Papers

OMVPE Growth and Characterization of InAsBi and InAsSbBi, K.Y. Ma, D.H. Jaw, Z.M. Fang, R.M. Cohen, and G.B. Stringfellow, U.S. Workshop on OMVPE, October, 1989, Monterey, CA.

OMVPE Growth and Characterization of Bi-containing III/V Alloys, 5th International Conference on MOVPE, Aachen, Germany, June 1990.

Study of Bi-containing III/V Semiconductors for Infrared Device Applications, Electronic Materials Conference, Santa Barbara, June 1990.

Decomposition Mechanisms of Antimony Source Compounds for OMVPE, C.A. Larsen, R.W. Gedridge, S.H. Li and G.B. Stringfellow, Paper E5.29, MRS Fall Meeting, November 26, 1990, Boston.

Pyrolysis Studies of Novel Sb Precursors, S.H. Li, C.A. Larsen, G.B. Stringfellow, and R.W. Gedridge, Paper VII.1, 5th Workshop on OMVPE, April 14, 1991, Panama City, Florida.

The Use of Triisopropylantimony for the Growth of InSb and GaSb by OMVPE, C.H. Chen, Z.M. Fang, G.B. Stringfellow, and R.W. Gedridge, Paper VII.5, 5th Workshop on OMVPE, April 14, 1991, Panama City, Florida.

j. Honors

G.B. Stringfellow, Institute of Electrical and Electronic Engineers (IEEE) Fellow, January 1990. (Involves support from ONR as well as DOE, AFOSR, ARO, NSF, and others).

G.B. Stringfellow, Distinguished Research Award, University of Utah, June 1990. (Involves support from ONR as well as DOE, AFOSR, ARO, NSF, and others).

- G.B. Stringfellow, Program and Publication Chairman, 18th International Symposium on GaAs and Related Compounds, Seattle, September, 1991.
- G.B. Stringfellow, Editorial Board, Materials Letters, 1989-present
- G.B. Stringfellow, Associate Editor, Journal of Crystal Growth, 1979-present.
- G.B. Stringfellow, Editorial Board, Journal of Electronic Materials, 1979-present.
- G.B. Stringfellow, Organizing Committee and Proceedings Chairman, 6th International Conference on MOVPE, Boston, June 1992.
- G.B. Stringfellow, International Advisory Committee, First International Symposium on Atomically Controlled Surfaces and Interfaces, Tokyo, Japan, November, 1992.
- G.B. Stringfellow, Program Committee, 10th International Conference on Crystal Growth, San Diego, CA, August 16-22, 1992.
- G.B. Stringfellow, International Advisory Board, International Conference on Vapor Growth and Epitaxy, Nagoya, Japan, July, 1991.
- G.B. Stringfellow, International Advisory Committee, 3rd International Conference on Chemical Beam Epitaxy, University of Oxford, 1-5 September, 1991.
- G.B. Stringfellow, International Advisory Committee, 5th International Conference on MOVPE, Aachen, Germany, June 1990.

k. Number of Graduate Students Receiving Support on ONR Grant

5 PhD students supported more than 25%.

Part II

Principal Investigator: G.B. Stringfellow

Cognizant ONR Scientific Officer: Dr. Mark Ross

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Description of Project:

The major goal of the project is the organometallic vapor phase epitaxial (OMVPE) growth of a new III/V alloy, InAsSbBi, with a band gap of <0.1 eV at 77°K, expected to be useful for infrared detectors with response extending to 12 microns. The alloy is metastable, but under the correct growth conditions we expect to be able to grow it by OMVPE. This apparently requires low growth temperatures of 250-350°C. Thus, new organometallic As and Sb precursors are being developed which pyrolyze at lower temperature than AsH₃ and TMSb, the normal group V sources. In addition, Bi precursors must be synthesized.

Significant Results:

During the last 3 years, the project has concentrated on the low temperature growth of InAs, InAsBi, InSb, InSbBi, InAsSb, and InAsSbBi. Bi has been added to InAs with concentrations as high as 6.1%. *This is sufficient to reduce the band gap to <0.1 eV.* The high Bi concentrations were obtained only by decreasing the growth temperature to 275°C. This necessitates the development and exploration of new group III and group V precursor molecules that give acceptable carbon contamination levels for low temperature growth. The new precursors will be described briefly, followed by the OMVPE growth results.

Evaluation of a new As source from ATM, DMAs, has been completed. Unfortunately, the 2 methyl radicals and single H radical result in increased carbon doping of the GaAs layers. In addition, Bi has been added to InAs, InSb, and InAsSb alloys using TMBi synthesized and purified by ATM.

Several new Sb sources have been tested for OMVPE growth, including triisopropylantimony (TIPSb), trivinylantimony (TVSb), and triallylantimony (TASb). TVSb pyrolyzes at approximately the same rate as TMSb, thus it offers little improvement for low temperature growth.

TASb pyrolyzes at much lower temperatures; however, we have not been successful in obtaining good morphologies using this Sb precursor. The most promising precursor is TIPSb. It pyrolyzes at temperatures about 200°C lower than for TMSb in a flow-tube reactor and has been successfully used for the growth of high quality layers of both GaSb and InSb. An additional advantage of TIPSb, as compared to TMSb, is the freedom from methyl radicals during growth. The importance of reducing carbon contamination is discussed later in this section.

In terms of OMVPE growth, the research InAsSb has led to the discovery of ordering in these materials. This is a potentially important discovery, since ordering is known to lower the band gap of III/V alloys.

Bi concentrations as high as 6.1% have been measured in InAsBi layers, even though the solubility limit is only 0.025%. It has been demonstrated that the Bi is, indeed, incorporated onto the group V sublattice. The lattice constant increases linearly with Bi concentration. Very recently, photoluminescence has been measured from these Bi-containing alloys. This is significant because it allows us to measure the shrinkage of band gap with the addition of Bi. In addition, the presence of photoluminescence shows that the minority carrier properties are quite favorable for ultimate device fabrication. The PL results are supplemented with absorption measurement which show the identical shrinkage of band gap of 55 meV/%Bi for InAsBi alloys. At higher concentrations a liquid second phase consisting mainly of In and Bi is formed on the surface, which gives rise to VLS whiskers grown on the surface. Lower growth temperatures of 275°C are found to allow incorporation of Bi concentrations into the solid before this phenomenon is observed. However, the methyl radicals from trimethylindium (TMIn) gives rise to very high carbon concentrations (10^{19} cm^{-3}) in InAs and InAsBi grown at low temperatures (300°C). The carbon acts as a donor in InAs. The resulting high free electron concentrations fills the conduction band, giving a Burstein shift in the absorption edge. Thus, even though we believe the $\text{InAs}_{0.94}\text{Bi}_{0.06}$ layers have an intrinsic band gap of less than 0.1 eV, it cannot be demonstrated using optical techniques.

In an effort to both reduce the carbon concentration as well as to increase the low-temperature growth rate, ethyldimethylindium (EDMIn) was substituted for the TMIn, and tertiarybutylarsine was substituted for arsine. The preliminary results indicate that the growth rate is, indeed, increased

significantly ($>10\times$ at 350°C). However, we measure no reduction in the carbon contamination levels.

The OMVPE growth of InSbBi gives more problems with formation of a liquid phase on the surface. Lowering the growth temperature to 350°C , which necessitates using TESb rather than TMSb, is found to be necessary to incorporate even 1% Bi into the solid. InAsSbBi alloys with approximately 10% Sb and 1.5% Bi have also been grown. The PL results indicates that the band gap shrinkage is approximately $46\text{ meV}/\%\text{Bi}$ for these alloys.

Personnel:

5 graduate students have been supported by the ONR contract:

Kevin Ma, C. Harmsten, Kenny Chiu, D.H. Jaw, and Z.M Fang.

One of these (Fang) has completed the PhD degree and two others (Ma and Jaw) are currently writing their PhD theses.